REACTIONS OF PERHALOALKANES

By

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INTRODUCTION

Free radical addition of halo- and perhaloalkanes to unsaturated compounds provides an excellent synthetic route to higher haloalkanes which can be further allowed to react to give a number of products. Until about 1930 the study of free radicals was restricted almost exclusively to the reactions of radicals of the triphenylmethyl type in solution and to the reactions of a few hydrocarbon radicals in the gas phase. During World War II the requirements for materials with the unusual properties of chemical inertness and thermal stability generated a crash program on fluorocarbon research. In the last 20 years numerous fluorocarbon products have gained widespread recognition for applications such as: propellants, wetting agents, textile treating agents, pharmaceutical intermediates, lubricants, elastomers, adhesives, sealants, plastics, films, protective coatings and fire extinguishing agents.

The difficulty of preparing polyhalogenated aliphatic hydrocarbons in good yields with a minimum number of reaction steps has stimulated interest in the free radical additions of haloalkanes to olefins. A number of workers[1] have reported the addition of various haloalkanes to unsaturated compounds in the presence of peroxides, visible or

ultraviolet light. Tarrant and co-workers[2-5] synthesized a number of haloalkanes by treating dibromodifluoromethane, bromochlorodifluoromethane, 1,2-dibromo-2-chloro-1,1,2-trifluoroethane and 1,2-dichloro-2-iodo-1,1,2-trifluoroethane with olefins under free radical conditions. They converted these addition products into various unsaturated compounds by treating them with base, with zinc or with both. For example, they made 1,1,2-trifluorobutadiene by dehydrohalogenation and dehalogenation of the addition product of 1,2-dibromo-2-chloro-1,1,2-trifluoroethane with ethylene under free radical conditions. Although extensive studies have been made on the free radical additions of several halo-and perhaloalkanes to unsaturated compounds, very little is known about the additions of 1,1,1-trichloroperfluoropropane, 1,2-dibromoperfluoroethane, 1,2-dibromo-1,2-dichlorodifluoroethane, 1,2-dibromoperfluoropropane, 2,3-dibromoperfluorobutane, 1,2-dibromoperfluorocyclobutane, 1,2-diiodoperfluoroethane and a large number of others to unsaturated compounds. It was decided to explore the addition of various halo-and polyhaloalkanes to olefins under free radical conditions, with the purpose of preparing unsaturated compounds from their addition products through simple reactions like dehalogenation, dehydrohalogenation, etc.

The work reported here is concerned mainly with the study of the addition of various polyhaloalkanes to olefins under free radical conditions and the dehydrohalogenation of the various 1:1 addition products.

DISCUSSION

Benzoyl Peroxide Initiated Addition Reactions

Free radical additions to unsaturated compounds have been extensively investigated since Kharasch[6] first reported that carbon tetrachloride and chloroform reacted with 1-octene in the presence of free radicals to give 1,1,1,3-tetrachlorononane and 1,1,1-trichlorononane, respectively. Reactions of this type are believed to follow the mechanism proposed by Kharasch[7] as shown below, using bromotrichloromethane as the perhaloalkane.

$$R-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-R \xrightarrow{\Delta} R\cdot + RCOO\cdot + CO_2 \qquad (1)$$

$$R\cdot + CCl_3Br \longrightarrow RBr + \cdot CCl_3 \qquad (2)$$

$$Cl_3C\cdot + RCH{=}CH_2 \longrightarrow CCl_3CH_2\dot{C}HR \qquad (3)$$

$$CCl_3CH_2\dot{C}HR + CCl_3Br \longrightarrow CCl_3CH_2CHRBr + \cdot CCl_3 \qquad (4)$$

Homolytic scission of the carbon-bromine bond can also be accomplished by irradiation with ultraviolet light, in which case equations 1 and 2 would be replaced by equation 5.

$$CCl_3Br \xrightarrow{h\nu} \cdot CCl_3 + \cdot Br \qquad (5)$$

An interesting side reaction is frequently observed which results in the formation of higher molecular weight adducts known as telomers. The telomerization process is a result of the reaction of the intermediate radical, $CCl_3CH_2\dot{C}HR$, with the olefin as shown below.

$$CCl_3CH_2\dot{C}HR + CH_2{=}CHR \longrightarrow CCl_3CH_2CHRCH_2\dot{C}HR + nCH_2{=}CHR \longrightarrow CCl_3(CH_2CHR)_nCH_2\dot{C}HR \qquad (6)$$

$$CCl_3(CH_2CHR)_nCH_2\dot{C}HR + CCl_3Br \longrightarrow CCl_3(CH_2CHR)_nCH_2CHRBr + \cdot CCl_3 \qquad (7)$$

$$n = 0, 1, 2, 3\text{---}$$

The addition products with n = 0, 1, 2, 3--- are named the 1:1 adduct, 2:1 adduct, and 3:1 adduct, etc. Adducts with $n > 1$ are termed telomers. In general, in every free radical addition of a haloalkane to olefin, a few lower telomers are formed. Their proportions depend mainly on the reaction conditions and the relative reactivity of the intermediate radical, $CCl_3CH_2\dot{C}HR$, toward olefin and haloalkane.

A higher ratio of haloalkane to olefin will result in higher conversion of olefin to 1:1 adduct because the radical, $CCl_3CH_2\dot{C}HR$, will have a higher probability of colliding with a molecule of perhaloalkane than with a molecule of olefin. Sometimes ratios of haloalkane to olefin as

high as 10:1 are needed to obtain a significant yield of 1:1 adduct. A lower ratio of haloalkane to olefin is desired whenever one needs a high yield of 2:1 and 3:1 adducts. Hanford[8] obtained the 1:1, 2:1, and 3:1 adducts in 8.7, 57, and 24% yields, respectively, from the addition of CCl_4 to excess ethylene in an autoclave at 1650 -1750 psi and 95-100° C.

The relative reactivity of the intermediate radical, $CCl_3CH_2\dot{C}HR$, toward olefin and perhaloalkane plays a very important role in determining the reaction path. The importance of the relative reactivity of the intermediate radical, $CCl_3CH_2\dot{C}HR$, towards olefin and haloalkane can be demonstrated from the results of the reaction of CCl_4 and CCl_3Br with ethylene. Kharasch[7] obtained a 95% yield of 1:1 adduct in the addition of CCl_3Br to ethylene while Hanford[8] obtained only 8.7% yield of 1:1 adduct in the addition of CCl_4 to ethylene. The intermediate radical, $CCl_3CH_2\dot{C}H_2$, is more reactive towards CCl_3Br than CCl_4 due to the 19 kcal. energy difference of the C—Br and the C—Cl bond. The radical, $CCl_3CH_2\dot{C}H_2$, is more reactive towards ethylene than CCl_4 but is very much less reactive towards ethylene than CCl_3Br.

Another side reaction which is often observed is the decay of the radical into another radical and olefin.

Lovelace[9] observed the formation of $CCl_3CH=C(CH_3)_2$ in the addition of CCl_4 to isobutylene. According to him the intermediate radical, $CCl_3CH_2\dot{C}(CH_3)_2$, decays into olefin, $CCl_3CH=C(CH_3)_2$, and radical, H· .

Addition of $CF_3CF_2CCl_3$ and $CF_2ClCF_2CCl_3$ to Olefins and Dehydrohalogenation of the 1:1 Adducts

The only report in the literature of the addition of $CF_3CF_2CCl_3$ and $CF_2ClCF_2CCl_3$ to olefins was made by Bardalaye[10] in 1966 from this laboratory. His work followed the studies reported here and he added these perhaloalkanes to trimethylvinylsilane in the presence of benzoyl peroxide.

A detailed study on the addition of $CF_3CF_2CCl_3$ and $CF_2ClCF_2CCl_3$ to olefins in the presence of benzoyl peroxide was made. The addition of $CF_3CF_2CCl_3$ to ethylene was carried out by using a 0.7 molar ratio of $CF_3CF_2CCl_3$ to ethylene. The 1:1, 2:1, and 3:1 adducts were formed in 15, 21, and 10% yield. Only in this case were the 2:1 and 3:1 adducts isolated and identified. In all other cases no attempts were made to isolate and identify these 2:1 and 3:1 adducts.

The additions of $CF_3CF_2CCl_3$ (1.2 mole) and $CF_2ClCF_2CCl_3$ (1.2 mole) to propylene (1.0 mole) were separately carried out. In these cases gas chromatography of the reaction mixture showed patterns similar to that observed in the reaction of $CF_3CF_2CCl_3$ with ethylene. The 1:1 adducts

were obtained in slightly better yields. The amounts of 2:1 and 3:1 adducts were estimated by v.p.c. analysis. In the addition of $CF_3CF_2CCl_3$ to propylene the 2:1 and 3:1 adducts were formed in 8 and 12% yields, respectively, and in the addition of $CF_2ClCF_2CCl_3$ to propylene the same two adducts were formed in 12 and 10% yields.

The addition of $CF_3CF_2CCl_3$ and $CF_2ClCF_2CCl_3$ to isobutylene was carried out using a 3:1 ratio of perhaloalkane to isobutylene. Analytical gas chromatography of the reaction mixture did not show a clean pattern and this could be due to product decomposition at the high column temperature used (190° C.). Preparative scale gas chromatography of the reaction mixture at lower temperature and reduced pressure showed the presence of three new main products and showed nice clean patterns. Two of these products were identified in each case and the third, a very high boiling product, was discarded. These products were identified as the olefins, $CF_3CF_2CCl_2CH_2C(CH_3)=CH_2$ and $CF_2ClCF_2CCl_2CH_2C(CH_3)=CH_2$, and the 1:1 adducts, $CF_3CF_2CCl_2CH_2CCl(CH_3)_2$ and $CF_2ClCF_2CCl_2CH_2CCl(CH_3)_2$. In the addition of $CF_3CF_2CCl_3$ to isobutylene the 1:1 adduct was the main product, but with $CF_2ClCF_2CCl_3$, the olefin, $CF_2ClCF_2CCl_2CH_2C(CH_3)=CH_2$, was the main product.

The formation of the olefin in these additions can be explained by the following mechanism:

$$C_6H_5\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}C_6H_5 \xrightarrow{\Delta} C_6H_5\cdot + CO_2 + C_6H_5CO_2\cdot \qquad (1)$$

$$C_6H_5\cdot + R_fCCl_3 \longrightarrow C_6H_5Cl + R_f\dot{C}Cl_2 \qquad (2)$$

$$R_f\dot{C}Cl_2 + CH_2=C(CH_3)_2 \longrightarrow R_fCCl_2CH_2\dot{C}(CH_3)_2 \qquad (3)$$

$$R_fCCl_2CH_2\dot{C}(CH_3)_2 \longrightarrow \underset{A}{R_fCCl_2CH_2C(CH_3)=CH_2} \quad \text{or}$$

$$\underset{B}{R_fCCl_2CH=C(CH_3)_2} + H\cdot \qquad (4)$$

$$R_fCCl_2CH_2\dot{C}(CH_3)_2 + R_fCCl_3 \longrightarrow R_fCCl_2CH_2CCl(CH_3)_2 + R_f\dot{C}Cl_2 \qquad (5)$$

$$R_fCCl_2CH_2\dot{C}(CH_3)_2 + \text{olefin} \longrightarrow \longrightarrow \text{telomers} \qquad (6)$$

$$R_f = CF_3CF_2 \text{ or } CF_2ClCF_2$$

Lovelace[9] obtained $CCl_3CH=C(CH_3)_2$ in small amounts from the addition of CCl_4 to isobutylene in the presence of benzoyl peroxide. In the absence of v.p.c. and n.m.r. in those days, he established the structure by its hydrolysis to β-methylcrotonic acid. It was found in the addition of $CF_3CF_2CCl_3$ and $CF_2ClCF_2CCl_3$ to isobutylene in the presence of benzoyl peroxide that the olefin (A), $R_fCCl_2CH_2C(CH_3)=CH_2$, was the only isomer formed.

A number of products were formed in each case in the dehydrohalogenation of the following compounds with potassium hydroxide: $CF_2ClCF_2CCl_2CH_2CHClCH_3$, $CF_3CF_2CCl_2CH_2CCl(CH_3)_2$, $CF_2ClCF_2CCl_2CH_2CCl(CH_3)_2$, and $CF_2ClCF_2CCl_2CH_2C(CH_3)=CH_2$. For example, the addition product, $CF_2ClCF_2CCl_2CH_2CCl(CH_3)_2$, on dehydrohalogenation gave seven products. The first three could not be isolated and v.p.c. analysis indicated them to be the isomeric olefins, $CF_2ClCF_2CCl_2CH_2C(CH_3)=CH_2$, $CF_2ClCF_2CCl_2CH=C(CH_3)_2$, and $CF_2ClCF_2CCl=CHCCl(CH_3)_2$ while the other four were identified as $CF_2ClCF_2CCl=CHC(CH_3)=CH_2$, $CF_2ClCF_2CCl=C=C(CH_3)_2$, $CF_2ClCF_2C\equiv CCCl(CH_3)_2$ and $CF_2ClCF_2C\equiv CC(CH_3)=CH_2$. The isolation and identification of the isomeric olefins could not be achieved in most cases. Only one of them, $CF_2ClCF_2CCl=CHCHClCH_3$ was isolated and identified. The presence of the other isomeric olefins was suspected by their v.p.c. retention time.

The dehydrohalogenation products of $CF_2ClCF_2CCl_2CH_2CHClCH_3$ polymerized very easily and some polymerization occurred even during dehydrohalogenation. In the dehydrohalogenation of $CF_3CF_2CCl_2CH_2CCl(CH_3)_2$ only the allene was isolated pure and the other products were obtained in an impure state. No further attempts were made to isolate the other products because similar compounds were isolated from the dehydrohalogenation of $CF_2ClCF_2CCl_2CH_2CCl(CH_3)_2$ and $CF_2ClCF_2CCl_2CH_2C(CH_3)=CH_2$.

The allenes were formed in good yields and the dienes only in trace amounts in the dehydrohalogenation of $CF_3CF_2CCl_2CH_2CCl(CH_3)_2$ and $CF_2ClCF_2CCl_2CH_2CCl(CH_3)_2$. Also the -yne - enes were formed in better yields than the alkynes in these reactions. The dehydrohalogenation of olefin, $CF_2ClCF_2CCl_2CH_2(CH_3)=CH_2$, gave good yields of -diene and -yne-ene.

A number of workers[3,7,11-13] have added CCl_3Br, CF_3I, and $CF_2BrCFClBr$ to allyl chloride under free radical conditions and obtained high yields of 1:1 adducts. No addition products were formed in the addition of $CF_3CF_2CCl_3$ and $CF_2ClCF_2CCl_3$ to allyl chloride in the presence of benzoyl peroxide. These results are not very surprising when one compares the results of Tarrant and Lovelace.[2] They found that CF_2ClBr and CF_2Br_2 do not react with chloroölefins under the conditions used for reactions of hydrocarbon olefins. Undoubtedly, the mechanism postulated by Kharasch for the peroxide catalyzed reaction of bromotrichloromethane to olefins is operative in these reactions.

$$R_fCCl_3 + (C_6H_5CO_2)_2 \longrightarrow R_f\dot{C}Cl_2 + C_6H_5Cl + C_6H_5CO_2 + CO_2 \qquad (1)$$

$$R_f\dot{C}Cl_2 + CH_2{=}CHCH_2Cl \longrightarrow R_fCCl_2CH_2\dot{C}HCH_2Cl \qquad (2)$$

$$R_fCCl_2CH_2\dot{C}HCH_2Cl + R_fCCl_3 \not\longrightarrow R_fCCl_2CH_2CHClCH_2Cl + R_f\dot{C}Cl_2 \qquad (3)$$

$R_f = CF_3CF_2$, CF_2ClCF_2.

Obviously one of the steps in the reactions is not being completed. It seems likely that step 1 is carried out since benzoyl peroxide is capable of initiating reaction with hydrocarbon olefins. The trichloromethyl radical must attack the double bond of a chloroölefin and it appears unlikely that $CF_3CF_2\dot{C}Cl_2$ and $CF_2ClCF_2\dot{C}Cl_2$ radicals would be any less reactive. If such is the case, then it follows that the chain-breaking step is step (3), and this results because of the inability of the secondary radical containing chlorine to remove a chlorine atom from the $CF_3CF_2CCl_3$ or $CF_2ClCF_2CCl_3$.

The addition of $CF_3CF_2CCl_3$ to chlorotrifluoroethylene gave a small amount of white polymeric material. No 1:1 addition product was formed. Here again the chain-breaking step is step (3).

Addition of $C_6H_5CCl_3$ and $CFCl_2CFCl_2$ to Ethylene

There are no reports in the literature on the addition of $C_6H_5CCl_3$ and $CFCl_2CFCl_2$ to olefins under free radical conditions. A study was made of the addition of $C_6H_5CCl_3$ and $CFCl_2CFCl_2$ to ethylene in the presence of benzoyl peroxide. It was found that they do not give any addition products under the conditions employed.

Addition of CCl_3Br to Hexafluorocyclobutene, Chlorotrifluoroethylene and Tetrafluoroethylene

Bromotrichloromethane reacts with a number of unsaturated compounds in the presence of peroxide or ultraviolet light to give adducts in fair to good yields.[1a] The reaction of bromotrichloromethane with chlorotrifluoroethylene was first reported by Henne who claimed a 45% yield of a product which was first assumed to have the structure III[14] but was subsequently assigned the structure IV.[15,16] Similar results were obtained in this laboratory.

$CCl_3CClFCF_2Br$ — III

$CCl_3CF_2CFClBr$ — IV

There are no reports in the literature on the addition of bromotrichloromethane to perfluorocyclobutene and tetrafluoroethylene. It was found that bromotrichloromethane does not react with perfluorocyclobutene in the presence of benzoyl peroxide, but it does react with tetrafluoroethylene under the same conditions to give a 58% and 10% yield of 1:1 and 2:1 adduct, respectively. The 2:1 adduct was not isolated but its yield was estimated by v.p.c. analysis.

$$CCl_3Br + CF_2=CF_2 \longrightarrow CCl_3CF_2CF_2Br + CCl_3(CF_2CF_2)_2Br$$

Addition of $CCl_3CF_2CFClBr$ and $CCl_3CF_2CF_2Br$ to Ethylene and Dehydrohalogenation of $CCl_3CF_2CFClCH_2CH_2Br$

The addition of $CCl_3CF_2CFClBr$ and $CCl_3CF_2CF_2Br$ to ethylene was carried out to compare the reactivities of the end groups $-CCl_3$, $-CFClBr$, and $-CF_2Br$ towards radical abstraction of chlorine and bromine. It was found that the addition of $CCl_3CF_2CFClBr$ to ethylene gave only one product, $CCl_3CF_2CFClCH_2CH_2Br$, and none of the isomeric product, $CFClBrCF_2CCl_2CH_2CH_2Cl$, was formed. The addition of $CCl_3CF_2CF_2Br$ to ethylene gave four main products, $CCl_3CF_2CF_2CH_2CH_2Cl$, $CF_2BrCF_2CCl_2CH_2CH_2Cl$ (not positively identified - see below), $CCl_3CF_2CF_2CH_2CH_2Br$, and $CF_2BrCF_2CCl_2CH_2CH_2Br$ in 7, 1.5, 40, and 9% yields, respectively.

The second product, which could not be isolated, had a v.p.c. retention time between those of $CCl_3CF_2CF_2CH_2CH_2Cl$ and $CCl_3CF_2CF_2CH_2CH_2Br$ which suggested that this product could be $CF_2BrCF_2CCl_2CH_2CH_2Cl$.

The following mechanism could explain the formation of these products:

$$C_6H_5\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}C_6H_5 \xrightarrow{\Delta} C_6H_5\cdot + CO_2 + C_6H_5CO_2\cdot \qquad (1)$$

$R\cdot = C_6H_5\cdot$

$$R\cdot + CCl_3CF_2CF_2Br \begin{cases} \xrightarrow{k_1} RCl + CF_2BrCF_2\dot{C}Cl_2 \\ \xrightarrow{k_1'} RBr + CCl_3CF_2\dot{C}F_2 \end{cases} \qquad (2)$$

$$CF_2BrCF_2\dot{C}Cl_2 + CH_2{=}CH_2 \xrightarrow{k_2} CF_2BrCF_2CCl_2CH_2\dot{C}H_2 \qquad (3)$$

$$CCl_3CF_2\dot{C}F_2 + CH_2{=}CH_2 \xrightarrow{k_2'} CCl_3CF_2CF_2CH_2\dot{C}H_2 \qquad (4)$$

$$CCl_3CF_2CF_2CH_2\dot{C}H_2 + CCl_3CF_2CF_2Br \begin{cases} \xrightarrow{k_3} CCl_3CF_2CH_2CH_2Cl + CF_2BrCF_2\dot{C}Cl_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad (I) \\ \xrightarrow{k_3'} CCl_3CF_2CF_2CH_2CH_2Br + CCl_3CF_2\dot{C}F_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad (III) \end{cases} \qquad (5)$$

$$CF_2BrCF_2CCl_2CH_2\dot{C}H_2 + CCl_3CF_2CF_2Br \begin{cases} \xrightarrow{k_4} CF_2BrCF_2CCl_2CH_2CH_2Cl + CF_2BrCF_2\dot{C}Cl_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (II) \\ \xrightarrow{k_4'} CF_2BrCF_2CCl_2CH_2CH_2Br + CCl_3CF_2\dot{C}F_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (IV) \end{cases} \qquad (6)$$

It is reasonable to make the following approximations:

(a) $k_1 = k_3 = k_4 = k$ and $k_1' = k_3' = k_4' = k'$

(b) $k_2 = k_2'$

If the above approximations are made then the rate of formation of products I and III will be proportional to the concentration of radical, $CCl_3CF_2CF_2CH_2\dot{C}H_2$. Similarly, the rate of formation of products II and IV will be proportional to the concentration of radical, $CF_2BrCF_2CCl_2CH_2\dot{C}H_2$. The relative reactivities of $-CCl_3$ and $-CF_2Br$ end groups towards radical abstraction of chlorine and bromine will be the ratio of amount of product I formed to the amount of product III formed or the amount of product II formed to the amount of product IV formed. From these studies it appears that $-CF_2Br$ end group is at least six times more reactive than $-CCl_3$ end group for radical abstraction of bromine and chlorine (see p.49). Tarrant and Gillman[3] obtained only $CF_2BrCFClCH_2CHBrCH_3$ in the addition of $CF_2BrCFClBr$ to propylene in the presence of benzoyl peroxide and none of the other isomer, $CFClBrCF_2CH_2CHBrCH_3$, was obtained. The reactivities of $-CCl_3$, $-CF_2Br$, and $-CFClBr$ towards radical abstraction of chlorine and bromine were found to be in the order $-CFClBr \gg -CF_2Br > -CCl_3$ in compounds, $CCl_3CF_2CFClBr$ and $CCl_3CF_2CF_2Br$.

The dehydrohalogenation of $CCl_3CF_2CF_2CH_2CH_2Br$ with potassium hydroxide gave only one olefin, $CCl_3CF_2CFClCH{=}CH_2$.

None of the other olefin, $CCl_3CF_2CF{=}CHCH_2Br$, or the allene, $CCl_3CF_2CF{=}C{=}CH_2$, was formed.

Addition of $CF_2BrCFClBr$ to Acrylonitrile

The addition of $CF_2BrCFClBr$ to olefins was studied by a number of workers[1b] chiefly in this laboratory. Heiba[11] and Kharasch[17] have added CCl_3Br to allyl cyanide and obtained a good yield of 1:1 adduct. Haszeldine[21] added CF_3I to acrylonitrile at 200° C. and obtained a 72% yield of 1:1 adduct, CF_3CH_2CHICN. There are no reports in the literature on the radical addition of $CF_2BrCFClBr$ to acrylonitrile. This reaction was attempted in the presence of benzoyl peroxide but it was found that acrylonitrile polymerized and no 1:1 adduct seemed to be formed.

Addition of $CFClBrCFClBr$ to Ethylene

There are no reports in the literature on the radical addition of $CFClBrCFClBr$ to olefins. It was thought that $CFClBrCFClBr$ would behave in a manner similar to $CF_2BrCFClBr$ in radical addition to olefins in that the addition would take place in both directions to give the 2:1 adduct, $CH_2BrCH_2CFClCFClCH_2CH_2Br$. This adduct should be converted easily to the 1,3,5-triene, $CH_2{=}CHCF{=}CF{-}CH{=}CH_2$.

It was found that a considerable amount of debromination occurred to give the olefin, $CFCl=CFCl$, and that the addition occurred only in one direction to give a 30% yield of $CFClBrCFClCH_2CH_2Br$. The high boiling residue consisted mostly of the 2:1 adduct, $CFClBrCFClCH_2CH_2CH_2CH_2Br$ which was identified as follows. The high boiling residue was dehalogenated and the olefin produced was dehydrohalogenated. Elemental analysis showed the presence of chlorine in this compound. Infrared spectroscopy showed a strong C=C absorption at 5.80μ which was due to $CFCl=CF-$ as compared with C=C absorption at 5.76μ in $CFCl=CFCH_2CH_2Br$.

The 1:1 adduct was converted into olefins, $CFCl=CFCH_2CH_2Br$ and $CFClBrCFClCH=CH_2$ by dehalogenation and dehydrohalogenation, respectively. The olefin, $CFCl=CFCH_2CH_2Br$, on dehydrohalogenation gave the diene, $CFCl=CF-CH=CH_2$, which polymerizes on standing at room temperature and at 10° C. This product can be stored at liquid N_2 temperature with little or no polymerization.

Addition of CF_2BrCF_2Br, $CF_3CFBrCF_2Br$, $CF_3CFBrCFBrCF_3$, $CF_3CFBrCClBrCF_3$, 1,2-Dibromoperfluorocyclobutane, and $CF_2BrCFHBr$ to Olefins

There are no reports in the literature on the radical addition of CF_2BrCF_2Br, $CF_3CFBrCF_2Br$, $CF_3CFBrCFBrCF_3$, 1,2-dibromoperfluorocyclobutane, or $CF_2BrCFHBr$ to olefins.

A study on the addition of CF_2BrCF_2Br, $CF_3CFBrCF_2Br$, and 1,2-dibromoperfluorocyclobutane to vinyltrimethylsilane in the presence of benzoyl peroxide was made by Bardalaye[10] in 1966 in this laboratory following the results of my studies on the addition of these alkanes to olefins.

The addition of CF_2BrCF_2Br to ethylene gave good yields of 1:1 and 2:1 adducts. Dehydrohalogenation of 1:1 adduct, $CF_2BrCF_2CH_2CH_2Br$, gave the olefin, $CF_2BrCF_2CH=CH_2$, in good yield, while the dehydrohalogenation of 2:1 adduct, $CF_2BrCF_2CH_2CH_2CH_2CH_2Br$ (in ethanol), gave a good yield of the ether, $CF_2BrCF_2CH_2CH_2CH_2CH_2-O-CH_2CH_3$, and a poor yield of the expected olefin, $CF_2BrCF_2CH_2CH_2CH=CH_2$. No 1:1 adducts were formed in the addition of CF_2BrCF_2Br to chlorotrifluoroethylene and to allyl ethyl ether.

A good yield of 1:1 adduct was isolated in the addition of $CF_3CFBrCF_2Br$ to ethylene, but no 1:1 adducts were formed in its addition to either allyl chloride or to allyl ethyl ether. The 1:1 adduct of the former reaction was identified as $CF_2BrCF(CF_3)CH_2CH_2Br$ rather than the other isomeric product, $CF_3CFBrCF_2CH_2CH_2Br$. Dehydrohalogenation of $CF_2BrCF(CF_3)CH_2CH_2Br$ gave a good yield of the olefin, $CF_2BrCF(CF_3)CH=CH_2$.

No 1:1 adducts were formed in the addition of $CF_3CFBrCFBrCF_3$ or $CF_3CFBrCClBrCF_3$ to ethylene in the presence of benzoyl peroxide. A considerable amount of debromination occurred in each case similar to that which

took place in the addition of CFClBrCFClBr to ethylene (see p.51). It appears that the radicals, $CFClBr\dot{C}FCl$, $CF_3CFBr\dot{C}FCF_3$, and $CF_3CFBr\dot{C}ClCF_3$, are sterically hindered and that they decay very fast into olefin and bromine radical. Although CFCl=CFCl can easily be brominated without u.v. light, $CF_3CF=CFCF_3$ and $CF_3CF=CClCF_3$ brominate only in the presence of u.v. light and $CF_3CCl=CClCF_3$ does not brominate even in the presence of u.v. light.

1,2-Dibromoperfluorocyclobutane and $CF_2BrCFHBr$ do not add to olefins in the presence of benzoyl peroxide.

Addition of $CH_2=CHI$ to Tetrafluoroethylene

Park and co-workers[18,19] added $CF_2=CHI$, $CF_2=CClI$, and $CF_2=CFI$ to a number of hydrocarbon and fluoroölefins and obtained good yields of 1:1 adducts. There are no reports in the literature on the addition of vinyl iodide to tetrafluoroethylene. It was found that vinyl iodide does not add to tetrafluoroethylene in the presence of benzoyl peroxide.

Addition of CF_2ICF_2I to Olefins

Recently Knunyants and co-workers[20] have reported the addition of CF_2ICF_2I to ethylene. They claim that they obtained an 80% yield of 1:1 adduct and a 7.9% yield of 2:1 adduct. When this work was reported in this

laboratory under similar conditions, no 1:1 and 2:1 adducts were obtained; only black, solid, polymeric material was observed. The addition of CF_2ICF_2I to ethylene and to allyl chloride was attempted in the presence of benzoyl peroxide. In the addition of CF_2ICF_2I to ethylene a new product was shown by v.p.c. to be present in less than 2% yield. This product on dehydrohalogenation gave a low boiling product which could not be isolated and identified. No adduct was obtained in the addition of CF_2ICF_2I to allyl chloride.

Addition of $CH_2=CHCH_2I$ to Tetrafluoroethylene

Kharasch and Sage[17] have observed unexpected products in the addition of CCl_3Br to allyl bromide, which they explained on the basis of β elimination of a halogen atom from an intermediate radical. They proposed the following scheme:

$$CCl_3Br \xrightarrow{h\nu} \cdot CCl_3 + Br\cdot \quad (1)$$

$$Cl_3C\cdot + CH_2=CH-CH_2Br \longrightarrow CCl_3CH_2-\dot{C}HCH_2Br \quad (2)$$

$$CCl_3CH_2-\dot{C}HCH_2Br \longrightarrow \underset{I}{CCl_3CH_2-CH=CH_2} + Br\cdot \quad (3)$$

$$CCl_3CH_2-CH=CH_2 + \cdot CCl_3 \longrightarrow CCl_3CH_2-\dot{C}H-CH_2CCl_3 \quad (4)$$

$$CCl_3CH_2\dot{C}HCH_2CCl_3 + CCl_3Br \longrightarrow \underset{II}{CCl_3CH_2CHBrCH_2CCl_3} + \cdot CCl_3 \quad (5)$$

$$Br\cdot + CH_2=CHCH_2Br \longrightarrow CH_2Br\dot{C}HCH_2Br \quad (6)$$

$$CH_2Br\dot{C}HCH_2Br + CCl_3Br \longrightarrow \underset{III}{CH_2BrCHBrCH_2Br} + \cdot CCl_3 \quad (7)$$

Compounds II and III were obtained as major products when excess CCl_3Br was used, but compound I was obtained rather than compound II when excess of allyl bromide was used. They did not consider the possibility of the formation of allyl and bromine radicals from allyl bromide. The allyl radical will form allyl bromide by bromine abstraction from CCl_3Br and will give only traces of 1,5-hexadiene. There are no reports in the literature on the addition of either allyl bromide or allyl iodide to olefins. A study was made on the addition of allyl iodide to tetrafluoroethylene in the presence of benzoyl peroxide. A large amount of iodine was present in the residual reaction mixture and four main products, CH_3CHICH_3, $(CH_2=CHCH_2CF_2\dot{}_2$, $CH_2=CHCH_2CFCF_2I$, and CF_2ICF_2I, were obtained. The allyl radicals were formed in high concentration due to the weak allylic C–I bond and the high resonance energy of the allyl radical.

The following mechanism could explain the formation of these products:

$$C_6H_5\overset{O}{\overset{\|}{C}}-O-O\overset{O}{\overset{\|}{C}}C_6H_5 \longrightarrow C_6H_5\cdot + CO_2 + C_6H_5CO_2\cdot \qquad (1)$$

$$C_6H_5\cdot + CH_2=CHCH_2I \longrightarrow CH_2=CH\dot{C}H_2 + C_6H_5I \qquad (2)$$

$$CH_2=CHCH_2I \xrightarrow{\Delta} CH_2=CH\dot{C}H_2 + I\cdot \qquad (3)$$

$$2CH_2=CH\dot{C}H_2 \longrightarrow (CH_2=CHCH_2\dot{}_2 \qquad (4)$$

$$(CH_2=CHCH_2\dot{}\,)_2 + CH_2=CH\dot{C}H_2 \longrightarrow CH_2=CHCH_3 + CH_2=CH\dot{C}HCH_2CH=CH_2 \quad (5)$$

$$CH_2=CH\dot{C}HCH_2CH=CH_2 \longrightarrow CH_2=CHCH=CHCH=CH_2 + H\cdot \quad (6)$$

$$CH_2=CHCH=CHCH=CH_2 \longrightarrow \text{Polymer} \quad (7)$$

$$H\cdot + CH_2=CHCH_2I \longrightarrow CH_3\dot{C}HCH_2I \longrightarrow CH_3CH=CH_2 + I\cdot \quad (8)$$

$$CH_2=CHCH_3 + H\cdot \longrightarrow CH_3\dot{C}HCH_3 \quad (9)$$

$$CH_3\dot{C}HCH_3 + CH_2=CHCH_2I \longrightarrow CH_3CHICH_3 + CH_2=CH\dot{C}H_2 \quad (10)$$

$$CH_2=CHCH_2\cdot + CF_2=CF_2 \longrightarrow CH_2=CHCH_2CF_2\dot{C}F_2 \quad (11)$$

$$CH_2=CHCH_2CF_2\dot{C}F_2 + CH_2=CHCH_2I \longrightarrow CH_2=CHCH_2CF_2CF_2I + CH_2=CH\dot{C}H_2 \quad (12)$$

$$CH_2=CHCH_2CF_2\dot{C}F_2 + CH_2=CH\dot{C}H_2 \longrightarrow (CH_2=CHCH_2CF_2\dot{}\,)_2 \quad (13)$$

$$CF_2=CF_2 + I\cdot \longrightarrow CF_2I\dot{C}F_2 \quad (14)$$

$$CF_2I\dot{C}F_2 + CH_2=CHCH_2I \longrightarrow CF_2ICF_2I + CH_2=CH\dot{C}H_2 \quad (15)$$

The H^1 and F^{19} N.M.R. Spectra of the New Compounds Prepared

F^{19} n.m.r. spectra

The F^{19} n.m.r. spectra of the compounds with the CF_3CF_2- group showed the presence of two chemically

shifted peaks, in the area ratio of 3:2, which did not show any fine structure.

The peak at lower field was assigned to CF_3- and that at higher field to $-CF_2-$.

The compounds with the CF_2ClCF_2- group also showed the presence of two chemically shifted peaks in the area ratio of 1:1. These peaks were not resolved in compounds where CF_2ClCF_2- group was attached to a saturated carbon, but were resolved into triplets in compounds where CF_2ClCF_2- was attached to an unsaturated carbon. The J_{F-F} values were larger for compounds with CF_2ClCF_2- group attached to triple bonded carbon than to a double bonded carbon.

The spectra of compounds with the CF_2BrCF_2- group showed the presence of two chemically shifted peaks in the area ratio of 1:1. These peaks showed the expected splitting in all compounds except in cases where CF_2BrCF_2- group was attached to a carbon which had two or more highly electronegative chlorine atoms as substituents.

The CF_2ICF_2- group in compound, $CF_2ICF_2CH_2CH{=}CH_2$, showed the presence of two peaks in the area ratio of 1:1 and each peak showed the expected splitting.

In compounds, $CCl_3CF_2CFClCH_2CH_2Br$ and $CCl_3CF_2CFClCH{=}CH_2$, the two $-CF_2-$ fluorines were magnetically non-equivalent, and they showed the expected splitting

The spectra of compound, $CCl_3CF_2CFClCH=CH_2$, showed some impurity which was suspected to be $CCl_3CFClCF_2CH=CH_2$.

The spectra of all other compounds showed the expected patterns.

H^1 n.m.r. spectra

The H^1 n.m.r. spectra of all compounds showed the expected patterns which in most cases were either too simple or too complex to warrant further discussion.

TABLE 1

H^1 and F^{19} N.M.R. Spectra of the New Compounds Prepared

Compd. No.	Assignment	Peak	Peak Area	Chemical Shift		Mult.[c]	J
				ppm (TFA)[a]	τ(TMS)[b]		(cps)
I	$CF_3CF_2CCl_2CH_2CH_2Cl$	A	1.46	-0.2	- -	S.N.R.	—
	A B D C	B	1.00	+39.2	- -	S.N.R.	—
		C	0.97	- -	6.21	3	8.0
		D	1.00	- -	7.25	3	8.0
II	$CF_3CF_2CCl_2(CH_2)_3CH_2Cl$	A	1.58	-1.3	- -	S.N.R.	—
	A B D C	B	1.00	+38.4	- -	S.N.R.	—
		C	1.00	- -	6.52	3	5.8
		D	3.00	- -	B	B	—
III	$CF_3CF_2CCl_2(CH_2)_5CH_2Cl$	A	1.60	-1.4	- -	S.N.R.	—
	A B D C	B	1.00	+38.5	- -	S.N.R.	—
		C	1.00	- -	6.56	3	6.4
		D	5.17	- -	- -	B	—
IV	$CF_3CF_2CCl_2CH_2CHClCH_3$	A	1.48	-2.01	- -	S.N.R.	—
	A B D C E	B	1.00	+38.4	- -	S.N.R.	—
		C	0.48	- -	5.36	6	7.02
		D	1.00	- -	7.04	3	6.32
		E	1.50	- -	8.12	2	7.0
V	$CF_3CF_2CCl_2CH_2C(CH_3)=CH_2$	A	1.53	-2.8	- -	S.N.R.	—
	A B D E C	B	1.00	+38.2	- -	S.N.R.	—
		C	1.01	- -	- -	M	—
		D	1.00	- -	7.31	1	—
		E	1.46	- -	8.24	1	—

TABLE 1 (continued)

Compd. No.	Assignment	Peak	Peak Area	Chemical Shift ppm (TFA)[a]	Chemical Shift τ(TMS)[b]	Mult.[c]	J (cps)
VI	$CF_3CF_2CCl_2CH_2CCl(CH_3)_2$ A B C D	A	1.46	+3.04	- -	S.N.R.	—
		B	1.00	+38.2	- -	S.N.R.	—
		C	1.00	- -	7.12	1	—
		D	3.06	- -	7.77	1	—
VII	$CF_3CF_2CCl=C=C(CH_3)_2$ A B C	A	1.54	+5.91	- -	S.N.R.	—
		B	1.00	+34.3	- -	S.N.R.	—
		C	- -	- -	8.50	1	—
VIII	$CF_2ClCF_2CCl_2CH_2CHClCH_3$ A B D C E	A	1.00	-17.07	- -	S.N.R.	—
		B	1.11	+31.26	- -	S.N.R.	—
		C	0.49	- -	5.53	6	6.46
		D	1.00	- -	7.22	3	5.92
		E	1.54	- -	8.30	2	6.56
IX	$CF_2ClCF_2CCl=CHCHClCH_3$ A B C D E	A	1.11	-9.1	- -	3	4.2
		B	1.00	+32.9	- -	3	4.1
		C	0.50	- -	3.65	2	5.4
		D	0.50	- -	5.29	5	—
		E	1.79	- -	8.54	2	3.3

TABLE 1 (continued)

Compd. No.	Assignment	Peak	Peak Area	Chemical Shift ppm (TFA)[a]	Chemical Shift τ(TMS)[b]	Mult.[c]	J (cps)
X	$CF_2ClCF_2CCl_2CH_2C(CH_3)=CH_2$ A B D E C	A	1.10	-17.1	- -	S.N.R.	——
		B	1.00	+31.1	- -	S.N.R.	——
		C	1.05	- -	5.02	C	——
		D	1.00	- -	7.10	1	——
		E	1.54	- -	8.16	1	——
XI	$CF_2ClCF_2CCl_2CH_2CCl(CH_3)_2$ A B C D	A	1.04	-18.2	- -	S.N.R.	——
		B	1.00	+30.8	- -	S.N.R.	——
		C	1.00	- -	7.10	1	——
		D	3.18	- -	8.09	1	——
XII	$CF_2ClCF_2C\equiv C-C(CH_3)=CH_2$ A B D C	A	1.00	-5.78	- -	3	7.57
		B	1.01	+20.03	- -	3	8.03
		C	1.00	- -	4.79	C	——
		D	1.51	- -	8.79	C	——
XIII	$CF_2ClCF_2CCl=CHC(CH_3)=CH_2$ A B C E D	A	1.00	-9.28	- -	3	4.06
		B	1.09	+31.72	- -	3	4.06
		C	0.47	- -	3.43	C	——
		D	1.00	- -	4.88	C	——
		E	1.35	- -	8.16	C	——

TABLE 1 (continued)

Compd. No.	Assignment	Peak	Peak Area	Chemical Shift ppm (TFA)[a]	Chemical Shift τ(TMS)[b]	Mult.[c]	J (cps)
XIV	$CF_2ClCF_2C{\equiv}C{-}CCl(CH_3)_2$ A B C	A	1.04	-6.63	- -	3	7.33
		B	1.00	+20.39	- -	3	7.32
		C	- -	- -	8.11	1	—
XV	$CF_2ClCF_2CCl{=}C{=}C(CH_3)_2$ A B C	A	1.01	-8.8	- -	3	4.76
		B	1.00	+29.6	- -	3	4.92
		C	- -	- -	8.23	1	—
XVI	$CCl_3CF_2CFClCH_2CH_2Br$ A B D C	A	1.00	+25.3	- -	2	3.64
		B	0.44	+33.9	- -	3,M	3.67
		C	- -	- -	6.02	C	—
		D	- -	- -	6.52	C	—
XVII	$CCl_3CF_2CFClCH{=}CH_2$ C,D E F	A	0.3	-15.7	- -	2,2	{8.6, 7.0
		B	0.5	+20.9	- -	2,2	{8.3,17.0 impurity}
		C	1.2	+25.3	- -	2,2	261, 2.8
		D	1.0	+28.5	- -	2,2	261, 9.3
		E	1.2	+42.5	- -	C	—
		F	- -	- -	- -	C.V.P.	—

TABLE 1 (continued)

Compd. No.	Assignment	Peak	Peak Area	Chemical Shift ppm (TFA)[a]	Chemical Shift τ(TMS)[b]	Mult.[c]	J (cps)
XVIII	$CCl_3CF_2CF_2Br$ (A B)	A	1.00	-22.9	- -	S.N.R.	—
		B	1.03	+25.7	- -	S.N.R.	—
XIX	$CCl_3CF_2CF_2CH_2CH_2Cl$ (A B D C)	A	0.96	+28.4	- -	M	—
		B	1.00	+31.5	- -	S.N.R.	—
		C	1.00	- -	6.2	3	8.0
		D	1.03	- -	- -	M	—
XX	$CCl_3CF_2CF_2CH_2CH_2Br$ (A B D C)	A	1.00	+28.3	- -	M	—
		B	1.05	+31.4	- -	S.N.R.	—
		C	1.02	- -	6.3	3	8.2
		D	1.01	- -	- -	M	—
XXI	$CF_2BrCF_2CCl_2CH_2CH_2Br$ (A B D C)	A	1.00	-22.3	- -	S.N.R.	—
		B	1.06	+27.8	- -	S.N.R.	—
		C	1.01	- -	6.1	3	8.0
		D	1.00	- -	6.9	3	8.0
XXII	$CFClBrCFClCH_2CH_2Br$ (A B D C)	A	1.00	-13.27	- -	2,2	18.7,5.04
		B	1.10	+33.8	- -	C	—
		C	1.00	- -	- -	C	—
		D	1.01	- -	- -	C	—

TABLE 1 (continued)

Compd. No.	Assignment	Peak	Peak Area	Chemical Shift ppm (TFA)[a]	Chemical Shift τ(TMS)[b]	Mult.[c]	J (cps)
XXIII	$CFClBrCFCl\underbrace{CH=CH_2}$	A	1.06	-12.35	- -	4	10.7
		B	1.00	+38.6	- -	M	——
		C	- -	- -	- -	C.V.P.	——
	A B C	X	- -	-22.7	1°	S.N.R.	impurity
XXIV	$CFCl=CFCH_2CH_2Br$	A	1.67	+28.3	- -	2,3	13.0, 2.05
		B	1.00	+45.4	- -	3	4.51
		C	1.17	+47.2	- -	3	4.51
	A D G H	D	1.87	+58.1	- -	2,3	13.3, 20.2
	cis 44%*	E	1.28	+68.0	- -	3	20.0
	$CFCl=CFCH_2CH_2Br$	F	1.08	+70.2	- -	3	20.0
	B,C E,F G H	G	- -	- -	- -	C	——
	trans 56%*	H	- -	- -	- -	C	——
XXV	$CFCl=CF\underbrace{CH=CH_2}$	A	1.64	+28.1	- -	2	11.0
		B	1.00	+43.2	- -	M	——
	A D G	C	1.19	+45.6	- -	M	——
	cis 44%*	D	1.51	+69.4	- -	2,2,3	11.3, 24.3, -
	$CFCl=CF\underbrace{CH=CH_2}$	E	1.19	+78.6	- -	2,M	24.7, ——
	B,C E,F G	F	1.00	+80.3	- -	2,M	24.3, ——
	trans 56%*	G	- -	- -	- -	C	——

TABLE 1 (continued)

Compd. No.	Assignment	Peak	Peak Area	Chemical Shift		Mult.[c]	J
				ppm (TFA)[a]	τ(TMS)[b]		(cps)
XXVI	$CF_2BrCF_2CH_2CH_2Br$ A B D C	A	1.00	-11.3	- -	3	3.6
		B	0.94	+34.7	- -	3,3	3.7, 16.2
		C	- -	- -	6.37	C	—
		D	- -	- -	7.28	C	—
XXVII	$CF_2BrCF_2(CH_2)_3CH_2Br$ A B D C	A	1.05	-12.7	- -	3	3.7
		B	1.00	+33.7	- -	3,3	3.4, 17.8
		C	1.00	- -	6.59	3	6.1
		D	3.08	- -	- -	—	—
XXVIII	$CF_2BrCF_2\underbrace{CH=CH_2}$ A B C	A	1.02	-11.0	- -	3	2.7
		B	1.00	+17.0	- -	3,2	2.7, 4.3
		C	- -	- -	- -	C.V.P.	—
XXIX	$CF_2BrCF_2(CH_2)_2\underbrace{CH=CH_2}$ A B D C	A	1.02	-12.4	- -	3	—
		B	1.00	+34.3	- -	3,3	2, 18.2
		C	1.44	- -	- -	C	—
		D	2.00	- -	- -	C.V.P.	—

TABLE 1 (continued)

Compd. No.	Assignment	Peak	Peak Area	Chemical Shift ppm (TFA)[a]	Chemical Shift τ(TMS)[b]	Mult.[c]	J (cps)
XXX	$CF_2BrCF_2(CH_2)_3\underbrace{CH_2OCH_2}_{C}CH_3$ A B D C E	A	1.04	-12.9	- -	3	3.4
		B	1.00	+33.7	- -	3,3	2.3, 5.0
		C	2.00	- -	- -	C	—
		D	3.11	- -	- -	C	—
		E	1.56	- -	9.03	3	7.0
XXXI	$CF_2BrCF(CF_3)CH_2CH_2Br$ A C B E D	A	2.15	-19.5	- -	5	11.85
		B	3.00	-3.5	- -	2,3	5.6, 10.8
		C	1.12	+97.9	- -	M	—
		D	1.10	- -	6.31	3	—
		E	1.00	- -	7.13	C	—
XXXII	$CF_2BrCF(CF_3)\underbrace{CH=CH_2}$ A C B D	A	1.00	-17.7	- -	5	11.1
		B	1.53	-1.9	- -	2,3	6.4, 10.6
		C	0.50	+101.2	- -	M	—
		D	- -	- -	- -	C.V.P.	—
XXXIII	$CF_2ICF_2CH_2-\underbrace{CH=CH_2}$ A B D C	A	1.03	-19.0	- -	3	4.6
		B	1.00	+28.5	- -	3,3	4.3, 17.3
		C	1.49	- -	- -	C.V.P.	—
		D	1.00	- -	8.24	3,2	17.5, 6.0

TABLE 1 (continued)

Compd. No.	Assignment	Peak	Peak Area	Chemical Shift ppm (TFA)[a]	Chemical Shift τ(TMS)[b]	Mult.[c]	J (cps)
XXXIV	$(\underset{B}{CH_2}=\underset{C}{CH}\underset{A}{CH_2}\underset{A}{CF_2})_2$	A	- -	+36.7	- -	C	——
		B	1.51	- -	- -	C	——
		C	1.00	- -	- -	C	——

a. Relative to trifluoroacetic acid (TFA).

b. Relative to tetramethylsilane (TMS).

c. 1^o = singlet, 2^o = doublet, 3^o = triplet, 4^o = quartet, 5^o = quintet, 6^o = sextet, B= broad, C = complex, C.V.P. = complex vinyl pattern, M = multiplet, S.N.R. = splitting not resolved.

* Estimated from area ratios and average values are given.

TABLE 2

Physical Properties of the New Compounds Prepared

Compd. No.	Compound	Yield %	b.p. °C./mm.	n_D^{21}	d_4^{21}	Analysis	
						Calcd.%	Found%
I	$CF_3CF_2CCl_2CH_2CH_2Cl$	15	33/10	1.3942	1.5225	Cl, 40.11	40.13
II	$CF_3CF_2CCl_2(CH_2)_3CH_2Cl$	21	78/9.5	1.4140	1.4461	Cl, 36.32	36.15
III	$CF_3CF_2CCl_2(CH_2)_5CH_2Cl$	10	67/0.6	1.4238	1.3625	Cl, 33.07	32.69
IV	$CF_3CF_2CCl_2CH_2CHClCH_3$	16	70/32	1.3970	1.4871	Cl, 38.10	37.91
V	$CF_3CF_2CCl_2CH_2C(CH_3)=CH_2$	10	45/6	1.3890	1.3819	Cl, 27.62	27.41
VI	$CF_3CF_2CCl_2CH_2CCl(CH_3)_2$	40	50/6	1.4065	1.4397	Cl, 36.28	36.12
VII	$CF_3CF_2CCl=C=C(CH_3)_2$	30	118.5(m)	1.3855	1.2594	Cl, 16.08	15.98
VIII	$CF_2ClCF_2CCl_2CH_2CHClCH_3$	20	47/2	1.4276	1.4902	Cl, 47.93	48.15
IX	$CF_2ClCF_2CCl=CHCHClCH_3$	—	156.5(m)	1.4096	1.4166	Cl, 41.04	40.73
X	$CF_2ClCF_2CCl_2CH_2C(CH_3)=CH_2$	25	172.5(m)	1.4421	1.4129	Cl, 38.95	38.62
XI	$CF_2ClCF_2CCl_2CH_2CCl(CH_3)_2$	13	47/0.5	1.4344	1.4301	Cl, 45.81	44.88
XII	$CF_2ClCF_2C{\equiv}C-C(CH_3)=CH_2$	31	109(m)	1.3975	1.1960	Cl, 17.69	17.62
XIII	$CF_2ClCF_2CCl=CH-C(CH_3)=CH_2$	41	152(m)	1.4273	1.3451	Cl, 29.95	29.96

TABLE 2 (continued)

Compd. No.	Compound	Yield %	b.p. °C./mm.	n_D^{21}	d_4^{21}	Analysis Calcd.%	Found%
XIV	$CF_2ClCF_2C{\equiv}C{-}CCl(CH_3)_2$	—	—	———	———	Cl, 29.95	29.54
XV	$CF_2ClCF_2CCl{=}C{=}C(CH_3)_2$	—	152.5(m)	1.4212	———	Cl, 29.95	30.08
XVI	$CCl_3CF_2CFClCH_2CH_2Br$	43	60/0.5	1.4801	1.8218	Br, 23.33	23.39
XVII	$CCl_2CF_2CFClCH{=}CH_2$	75	182(m)	1.4504	1.6357	Cl, 54.10	53.90
XVIII	$CCl_3CF_2CF_2Br$	58	134(m)	1.4301	1.9228	Br, 26.81	26.82
XIX	$CCl_3CF_2CF_2CH_2CH_2Cl$	7	187(m)	1.4297	———	F, 26.92	27.18
XX	$CCl_3CF_2CF_2CH_2CH_2Br$	40	209(m)	1.4486	1.8302	Br, 24.48	24.87
XXI	$CF_2BrCF_2CCl_2CH_2CH_2Br$	9	216(m)	1.4664	———	Br, 43.12	42.40
XXII	$CFClBrCFClCH_2CH_2Br$	30	53/2	1.4486	2.0020	Br, 50.16	49.98
XXIII	$CFClBrCFClCH{=}CH_2$	75	144(m)	1.4571	1.7209	Br, 33.30	33.29
XXIV	$CFCl{=}CFCH_2CH_2Br$	—	138(m)	1.4514	1.6808	Br, 38.94	38.82
XXV	$CFCl{=}CFCH{=}CH_2$	80	—	———	———	Cl, 27.68	28.29

TABLE 2 (continued)

Compd. No.	Compound	Yield %	b.p. °C./mm.	n_D^{21}	d_4^{21}	Analysis	
						Calcd.%	Found%
XXVI	$CF_2BrCF_2CH_2CH_2Br$	32	72/80	1.4167	1.9702	Br, 55.56	55.81
XXVII	$CF_2BrCF_2(CH_2)_3CH_2Br$	20	76/10	1.4337	1.7902	Br, 50.63	50.41
XXVIII	$CF_2BrCF_2CH=CH_2$	96	54.5	1.3556	1.6042	Br, 38.65	38.44
XXIX	$CF_2BrCF_2(CH_2)_2CH=CH_2$	14	119.5(m)	1.3851	———	Br, 34.02	33.22
XXX	$CF_2BrCF_2(CH_2)_3CH_2-OCH_2CH_3$	67	185.7(m)	1.3964	1.3670	Br, 28.48	28.34
XXXI	$CF_2BrCF(CF_3)CH_2CH_2Br$	51	145(m)	1.4017	1.9920	Br, 47.34	47.34
XXXII	$CF_2BrCF(CF_3)CH=CH_2$	54	79(m)	1.3469	1.6663	Br, 31.17	31.58
XXXIII	$CH_2=CHCH_2CF_2CF_2I$	34	114(m)	1.4188	1.8260	I, 47.78	47.65
XXXIV	$(CH_2=CHCH_2CF_2\rightarrow_2$	6	118(m)	1.3720	———	C, 52.75	52.33
						H, 5.49	5.31

(m) Micro determination

EXPERIMENTAL

General

All temperatures reported herein are uncorrected and are given in degrees Centigrade. Refractive indices were determined with an Abbé refractometer at the temperatures given. Densities were also determined at the temperatures listed, using either a one-milliliter or a five-milliliter pycnometer.

Infrared spectra were obtained using a Perkin-Elmer Infracord and a Beckman IR-10 and only those absorption peaks indicative of structural features are reported (in microns).

Vapor phase chromatographic separations were obtained using a silicon elastomer column with ca. 20% by weight of substrate on Chromosorb P. Helium was used as the carrier gas on the analytical chromatographs and nitrogen was used on the preparative model.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

A 300 ml. capacity autoclave was used in all experiments except in the addition of CCl_3Br to tetrafluoroethylene for which a 1.4 liter autoclave was used.

Nuclear magnetic resonance spectra were obtained on a Varian High Resolution Nuclear Magnetic Resonance Spectrometer operating at 60 megacycles for hydrogen spectra and at 56.4 megacycles for fluorine spectra. The interpretations were performed with the assistance of Dr. Wallace S. Brey, Jr., and only simple structural features are discussed. No data on complex spectra are given here, only their patterns are discussed. These are given in Table 1.

The reactants used were generally purchased from the normal commercial outlets or from Peninsular ChemResearch, Inc., Gainesville, Florida, and were not purified further.

Benzoyl Peroxide Initiated Addition Reactions

Addition of $CF_3CF_2CCl_3$ to Olefins and Dehydrohalogenation of the Addition Products

1. Addition to ethylene

A stainless steel autoclave (300 ml. capacity) was charged with $CF_3CF_2CCl_3$ (24.8 g., 1.05 mole) and benzoyl peroxide (5 g., 0.02 mole) and was cooled in liquid nitrogen. Ethylene (40 g., 1.43 mole) was vacuum transferred into the autoclave which was heated at 100° for 16 hours with constant rocking. The autoclave was cooled and vented. Low boiling material (22 g., mostly ethylene) was condensed.

Gas chromatography showed the presence of three new main products in the residual mixture. Distillation of the residual liquid yielded 25.6 g. (15% yield) of 1:1 adduct, $CF_3CF_2CCl_2CH_2CH_2Cl$, b.p. 33°/10 mm., n_D^{21} 1.3942, d_4^{21} 1.5225 (Anal. Calcd. for $C_5Cl_3F_5H_4$: Cl, 40.11. Found: Cl, 40.13%), 40 g. (21% yield) of 2:1 adduct, $CF_3CF_2CCl_2(CH_2)_3CH_2Cl$, b.p. 78°/9.5 mm., n_D^{21} 1.4140, d_4^{21} 1.4461 (Anal. Calcd. for $C_7Cl_3F_5H_8$: Cl, 36.32. Found: Cl, 36.15%) and 32 g. (10% yield) of 3:1 adduct, $CF_3CF_2CCl_2(CH_2)_5CH_2Cl$, b.p. 67°/0.6 mm., n_D^{21} 1.4238, d_4^{21} 1.3625 (Anal. Calcd. for $C_9Cl_3F_5H_{12}$: Cl, 33.07. Found: Cl, 32.69%). The H^1 and F^{19} n.m.r. spectra were consistent with the above structures.

2. Addition to propylene

$CF_3CF_2CCl_3$ (244 g., 1.03 mole), propylene (33 g., 0.86 mole) and benzoyl peroxide (5 g., 0.02 mole) were heated in an autoclave at 100° with constant rocking. On venting the autoclave 9.5 g. low boiling material (mostly propylene) was condensed. Gas chromatography showed the presence of three new main products in the residual mixture. Distillation yielded 25.2 g. (16% yield) of 1:1 adduct, $CF_3CF_2CCl_2CH_2CHClCH_3$, b.p. 70°/32 mm., n_D^{21} 1.3970, d_4^{21} 1.4871 (Anal. Calcd. for $C_6Cl_3F_5H_6$: Cl, 38.10. Found: Cl, 37.91%). The H^1 and F^{19} n.m.r. spectra were consistent with the above structure.

3. Addition to isobutylene

$CF_3CF_2CCl_3$ (381.6 g., 1.61 mole), isobutylene (27.5 g., 0.49 mole) and benzoyl peroxide (5 g., 0.02 mole) were heated in an autoclave at 100° for 16 hours with constant rocking. On venting the autoclave no gaseous material was obtained. Gas chromatography showed the presence of three new main products in the reaction mixture. Distillation yielded 13 g. (10% yield) of $CF_3CF_2CCl_2CH_2C(CH_3)=CH_2$, b.p. 45°/6 mm., n_D^{21} 1.3890, d_4^{21} 1.3819 (I.R. C=C 6.04μ) (Anal. Calcd. for $C_7Cl_2F_5H_7$: Cl, 27.62. Found: Cl, 27.41%) and 57.5 g. (40% yield) of 1:1 adduct, $CF_3CF_2CCl_2CH_2CCl(CH_3)_2$, b.p. 50°/6 mm., n_D^{21} 1.4065, d_4^{21} 1.4397 (Anal. Calcd. for $C_7Cl_3F_5H_8$: Cl, 36.28. Found: Cl, 36.12%). The H^1 and F^{19} n.m.r. spectra were consistent with the above structures.

4. Dehydrohalogenation of $CF_3CF_2CCl_2CH_2CCl(CH_3)_2$ with potassium hydroxide

$CF_3CF_2CCl_2CH_2CCl(CH_3)_2$ (20.6 g., 0.06 mole) was heated with KOH pellets (25 g., 0.45 mole) and the low boiling material (15 g.) distilled directly from the reaction mixture. Gas chromatography showed the presence of seven new main products in the reaction mixture. Only 4.4 g. (30% yield) of one of them was isolated pure and identified as $CF_3CF_2CCl=C<^{CH_3}_{CH_3}$, b.p. 118.5° (micro),

n_D^{21} 1.3855, d_4^{21} 1.2594 (I.R. C=C=C 5.07μ) (Anal. Calcd. for $C_7ClF_5H_6$: Cl, 16.08%. Found: Cl, 15.98%). The H^1 and F^{19} n.m.r. spectra were consistent with the above structure.

5. Addition to allyl chloride

$CF_3CF_2CCl_3$ (72 g., 0.3 mole), allyl chloride (15.3 g., 0.2 mole) and benzoyl peroxide (1 g., 0.004 mole) were heated in an autoclave at 95° for 5 hours. On venting the autoclave no low boiling material was obtained. Gas chromatography showed the absence of any high boiling material in the residual mixture.

6. Addition to chlorotrifluoroethylene

$CF_3CF_2CCl_3$ (215 g., 0.9 mole), chlorotrifluoroethylene (31 g., 0.3 mole) and benzoyl peroxide (1.5 g., 0.006 mole) were heated in an autoclave at 100° for 12 hours with constant rocking. On venting the autoclave 6 g. low boiling material (mostly chlorotrifluoroethylene) was condensed. Gas chromatography showed the absence of any high boiling material in the residual mixture.

Addition of $CF_2ClCF_2CCl_3$ to Olefins Dehydrohalogenation of the Addition Products

1. Addition to propylene

$CF_2ClCF_2CCl_3$ (266.5 g., 1.12 mole), propylene (42 g., 1 mole) and benzoyl peroxide (5 g., 0.02 mole) were heated

in an autoclave at 100° for 10 hours with constant rocking. On venting the autoclave 14 g. low boiling material (mostly propylene) was condensed. Gas chromatography showed the presence of three new main products in the residual mixture. Distillation yielded 42 g. (20% yield) of 1:1 adduct, $CF_2ClCF_2CCl_2CH_2CHClCH_3$, b.p. 47°/2 mm., n_D^{21} 1.4276, d_4^{21} 1.4902 (Anal. Calcd. for $C_6Cl_4F_4H_6$: Cl, 47.93. Found: Cl, 48.15%). The H^1 and F^{19} n.m.r. spectra were consistent with the above structure.

2. Dehydrohalogenation of $CF_2ClCF_2CCl_2CH_2CHClCH_3$ with potassium hydroxide

$CF_2ClCF_2CCl_2CH_2CHClCH_3$ (29 g., 0.1 mole) was dropped slowly to a mixture of KOH (11.2 g., 0.2 mole) and ethanol (23 g., 0.5 mole) at reflux temperature. It was kept for another 30 minutes at reflux temperature. The reaction mixture was poured into water and the organic layer was separated, washed and dried. Crude material (15 g.) was obtained. Gas chromatography showed the presence of seven new products in this crude material. Only one of them was isolated pure and identified as $CF_2ClCF_2CCl{=}CHCHClCH_3$, b.p. 156.5° (micro), n_D^{21} 1.4096, d_4^{21} 1.4166 (I.R. C=C 6.08μ) (Anal. Calcd. for $C_6Cl_3F_4H_5$: Cl, 41.04. Found: Cl, 40.73%). The H^1 and F^{19} n.m.r. spectra were consistent with the above structure.

3. Addition to isobutylene

$CF_2ClCF_2CCl_3$ (381 g., 1.5 mole), isobutylene (28 g., 0.5 mole) and benzoyl peroxide (5 g., 0.02 mole) were heated in an autoclave at 100° for 4 hours with constant rocking. On venting the autoclave no gaseous material was obtained. Gas chromatography showed the presence of three new main products in the reaction mixture. Distillation yielded 33.6 g. (25% yield) of $CF_2ClCF_2CCl_2CH_2C(CH_3)=CH_2$, b.p. 172.5° (micro), n_D^{21} 1.4421, d_4^{21} 1.4129 (I.R. C=C 6.06μ) (Anal. Calcd. for $C_7Cl_3F_4H_7$: Cl, 38.95. Found: Cl, 38.62%) and 20.42 g. (13% yield) of 1:1 adduct, $CF_2ClCF_2CCl_2CH_2CCl(CH_3)_2$, b.p. 47°/0.5 mm., n_D^{21} 1.4344, d_4^{21} 1.4301 (Anal. Calcd. for $C_7Cl_4F_4H_8$: Cl, 45.81. Found: Cl, 44.88%). The H^1 and F^{19} n.m.r. spectra were consistent with the above structure.

4. Dehydrohalogenation of $CF_2ClCF_2CCl_2CH_2C(CH_3)=CH_2$ with potassium hydroxide

$CF_2ClCF_2CCl_2CH_2C(CH_3)=CH_2$ (13.7 g., 0.05 mole) was heated with KOH pellets (11.2 g., 0.2 mole) and the low boiling material (7 g.) distilled directly from the reaction mixture. Gas chromatography showed the presence of two new main products, I (31% yield), II (41% yield) in the low boiling material. These were identified as follows:

I. $CF_2ClCF_2C{\equiv}C{-}C(CH_3)=CH_2$, b.p. 109° (micro), n_D^{21} 1.3975, d_4^{21} 1.1960 (I.R. C≡C 4.45μ, C=C 6.19μ) (Anal. Calcd. for $C_7ClF_4H_5$: Cl, 17.69. Found: Cl, 17.62%).

II. $CF_2ClCF_2CCl=CH-C(CH_3)=CH_2$, b.p. 152° (micro), n_D^{21} 1.4273, d_4^{21} 1.3451 (I.R. C=C 6.14μ, 6.24μ) (Anal. Calcd. for $C_7Cl_2F_4H_6$: Cl, 29.95. Found: Cl, 29.96%). The H^1 and F^{19} n.m.r. spectra were consistent with the above structure.

5. Dehydrohalogenation of $CF_2ClCF_2CCl_2CH_2CCl(CH_3)_2$ with potassium hydroxide

$CF_2ClCF_2CCl_2CH_2CCl(CH_3)_2$ (17.8 g., 0.06 mole) was heated with KOH pellets (20 g., 0.36 mole) and the low boiling material (11.5 g.) distilled directly from the reaction mixture. Gas chromatography showed the presence of five new main products in the reaction mixture. They were identified as follows:

I. $CF_2ClCF_2C\equiv C-C(CH_3)=CH_2$. Its properties are reported in the previous experiment.

II. $CF_2ClCF_2C\equiv C-CCl(CH_3)_2$ (I.R. C≡C 4.4μ) (Anal. Calcd. for $C_7Cl_2F_4H_6$: Cl, 29.95. Found: Cl, 29.54%).

III. $CF_2ClCF_2CCl=C=C(CH_3)_2$, b.p. 152.5° (micro), n_D^{21} 1.4212 (I.R. C=C=C 5.03μ) (Anal. Calcd. for $C_7Cl_2F_4H_6$: Cl, 29.95. Found: Cl, 30.08%).

IV and V, could not be separated pure, hence, they were not positively identified. V.p.c. analysis indicated IV to be $CF_2ClCF_2CCl_2CH_2CCH_3=CH_2$. The H^1 and F^{19} n.m.r. spectra were consistent with the above structure.

6. Addition to allyl chloride

$CF_2ClCF_2CCl_3$ (76 g., 0.3 mole), allyl chloride (15 g., 0.2 mole) and benzoyl peroxide (3 g., 0.012 mole) were heated in an autoclave at 95° for 5 hours with constant rocking. On venting the autoclave no gaseous material was obtained. Gas chromatography showed the absence of any higher boiling material in the reaction mixture.

Addition of $C_6H_5CCl_3$ to Ethylene

$C_6H_5CCl_3$ (300 g., 1.54 mole), ethylene (16 g., 0.57 mole) and benzoyl peroxide (5 g., 0.02 mole) were heated in an autoclave at 100° for 16 hours with constant rocking. On venting the autoclave 9 g. low boiling material (mostly ethylene) was condensed. Gas chromatography showed the absence of any higher boiling material in the residual mixture.

Addition of $CFCl_2CFCl_2$ to Ethylene

$CFCl_2CFCl_2$ (420 g., 2.06 mole), ethylene (15 g., 0.54 mole) and benzoyl peroxide (5 g., 0.02 mole) were heated in an autoclave at 100° for 16 hours with constant rocking. On venting the autoclave 6 g. low boiling material(mostly ethylene) was condensed. Gas chromatography showed the absence of any higher boiling material in the residual mixture.

Addition of CCl_3Br to Olefins

1. Addition to hexafluorocyclobutene

CCl_3Br (300 g., 1.5 mole), hexafluorocyclobutene (80 g., 0.5 mole) and benzoyl peroxide (2.5 g., 0.01 mole) were heated in an autoclave at 100° for 16 hours with constant rocking. On venting the autoclave 75 g. low boiling material (mostly hexafluorocyclobutene) was condensed. Gas chromatography showed the absence of any higher boiling material in the residual mixture.

2. Addition to chlorotrifluoroethylene

CCl_3Br (300 g., 1.5 mole), chlorotrifluoroethylene (60 g., 0.53 mole) and benzoyl peroxide (2.5 g., 0.01 mole) were heated in an autoclave at 100° for 4 hours. On venting the autoclave no gaseous material was obtained. Gas chromatography showed the presence of two new main products in the reaction mixture. Distillation yielded 79 g. (50% yield) of 1:1 adduct, $CCl_3CF_2CFClBr$, b.p. 63°/6 mm., n_D^{21} 1.4653 (Lit.[14] b.p. 58°-63°/6 mm., n_D^{20} 1.4673-1.4643). The F^{19} n.m.r. spectra was consistent with the above structure.

3. Addition to tetrafluoroethylene

CCl_3Br (1668 g., 8.4 mole), tetrafluoroethylene (200 g., 2.0 mole) and benzoyl peroxide (10.0 g., 0.04 mole) were heated in an autoclave (1.4 l. capacity) at

100° for 8 hours with constant rocking. On venting the autoclave 1 g. low boiling material (mostly tetrafluoroethylene) was condensed. Gas chromatography showed the presence of two new main products in the residual mixture. Distillation yielded 350 g. (58% yield) of 1:1 adduct, $CCl_3CF_2CF_2Br$, b.p. 134° (micro), n_D^{21} 1.4301, d_4^{21} 1.9228 (Anal. Calcd. for $C_3BrCl_3F_4$: Br, 26.81. Found: Br, 26.82%). The F^{19} n.m.r. spectra was consistent with the above structure.

Addition of $CCl_3CF_2CFClBr$ to Ethylene and Dehydrohalogenation of the Addition Product

1. Addition to ethylene

$CCl_3CF_2CFClBr$ (109 g., 0.35 mole), ethylene (4.2 g., 0.15 mole) and benzoyl peroxide (0.5 g., 0.002 mole) were heated in an autoclave at 100° for 3 hours with constant rocking. On venting the autoclave no gaseous material was obtained. Gas chromatography showed the presence of one new main product in the residual mixture. Distillation yielded 20 g. (43% yield) of 1:1 adduct, $CCl_3CF_2CFClCH_2CH_2Br$, b.p. 60°/0.5 mm., n_D^{21} 1.4801, d_4^{21} 1.8218 (Anal. Calcd. for $C_5BrCl_4F_3H_4$: Br, 23.33. Found: Br, 23.39%). The H^1 and F^{19} n.m.r. spectra were consistent with the above structure.

2. Dehydrohalogenation of $CCl_3CF_2CFClCH_2CH_2Br$ with potassium hydroxide

$CCl_3CF_2CFClCH_2CH_2Br$ (17 g., 0.05 mole), KOH (8 g., 0.14 mole) and ethanol (11.5 g., 0.25 mole) were heated in a 50 ml. flask fitted with water reflux condenser at reflux temperature for 30 minutes. The reaction mixture was poured into water and the organic layer was separated, washed and dried. Crude material (9 g., 75% yield) was obtained. Gas chromatography showed the presence of one new main product in this impure material. This was purified by preparative scale gas chromatography and identified as $CCl_3CF_2CFClCH=CH_2$, b.p. 182° (micro), n_D^{21} 1.4504, d_4^{21} 1.6357 (I.R. C=C 6.1μ) (Anal. Calcd. for $C_5Cl_4F_3H_3$: Cl, 54.10. Found: Cl, 53.90%). The H^1 and F^{19} n.m.r. spectra were consistent with the above structure.

Addition of $CCl_3CF_2CF_2Br$ to Ethylene

$CCl_3CF_2CF_2Br$ (325 g., 1.1 mole), ethylene (13 g., 0.46 mole) and benzoyl peroxide (2.5 g., 0.01 mole) were heated in an autoclave at 100° for 8 hours with constant rocking. On venting the autoclave no gaseous material was obtained. Gas chromatography showed the presence of four new main products in the reaction mixture. These were separated by distillation and preparative scale gas chromatography. Their amounts were estimated by v.p.c. analysis and were identified as follows:

I. $CCl_3CF_2CF_2CH_2CH_2Cl$ (8.6 g., 7% yield), b.p. 187° (micro), n_D^{21} 1.4297 (Anal. Calcd. for $C_5Cl_4F_4H_4$: C, 21.24; H, 1.42; F, 26.92; Br, 0.00. Found: C, 21.35; H, 1.46; F, 27.18, Br, 0.50%).

II was unidentified and could be $CF_2BrCF_2CCl_2CH_2CH_2Cl$ (2.3 g., 1.5% yield).

III. $CCl_3CF_2CF_2CH_2CH_2Br$ (60 g., 40% yield), b.p. 209° (micro), n_D^{21} 1.4486, d_4^{21} 1.8302 (Anal. Calcd. for $C_5BrCl_3F_4H_4$: Br, 24.48. Found: Br, 24.87%).

IV. $CF_2BrCF_2CCl_2CH_2CH_2Br$ (15 g., 9% yield), b.p. 216° (micro), n_D^{21} 1.4664 (Anal. Calcd. for $C_5Br_2Cl_2F_4H_4$: Br, 43.12. Found: Br, 42.40%). The H^1 and F^{19} n.m.r. spectra were consistent with the above structure.

Addition of $CF_2BrCFClBr$ to Acrylonitrile

$CF_2BrCFClBr$ (137 g., 0.5 mole), $CH_2=CHCN$ (13.5 g., 0.25 mole) and benzoyl peroxide (1 g., 0.004 mole) were heated in a Fischer-Porter tube at 100° for 2 hours. The reaction mixture was turned into a gel like solid mass which was filtered. The solid turned out to be a polymeric material while gas chromatography showed the absence of any higher boiling material in the filtrate.

Preparation and Addition of CFClBrCFClBr to Ethylene, Dehydrohalogenation and Dehalogenation of the Addition Product

1. Preparation of CFClBrCFClBr

CFClBrCFClBr was prepared by dechlorination of $CFCl_2CFCl_2$ followed by bromination of the olefin.

2. Addition to ethylene

CFClBrCFClBr (293 g., 1 mole), ethylene (20 g., 0.72 mole) and benzoyl peroxide (5 g., 0.02 mole) were heated in an autoclave at 100° for 16 hours with constant rocking. On venting the autoclave no gaseous material was obtained. Gas chromatography showed the presence of three new main products in the reaction mixture. These were separated by distillation and preparative scale gas chromatography. Their amounts were estimated by v.p.c. analysis and were identified as follows:

I. CFCl=CFCl (26.5 g., 20% yield), b.p. 22°, n_D^{21} 1.3763 (Lit.[22] b.p. 22°, n_D^0 1.3798).

II. CH_2BrCH_2Br (38 g., 20% yield), b.p. 131.2 (micro), n_4^{21} 1.5377, d_4^{21} 2.1647 (Lit.[23] b.p. 131.6, n_D^{25} 1.5379, d_4^{25} 2.1701).

III. $CFClBrCFClCH_2CH_2Br$ (85 g., 30% yield), b.p. 53°/2 mm., n_D^{21} 1.4486, d_4^{21} 2.0020 (Anal. Calcd. for $C_4Br_2Cl_2F_2H_4$: Br, 50.16. Found: Br, 49.98%). The H^1 and F^{19} n.m.r. spectra were consistent for the above compound III.

3. Dehydrohalogenation of $CFClBrCFClCH_2-CH_2Br$ with potassium hydroxide

$CFClBrCFClCH_2CH_2Br$ (10.3 g., 0.32 mole) was dropped slowly into a mixture of potassium hydroxide (5.6 g., 0.1 mole) and ethyl alcohol (4.6 g., 0.1 mole) at reflux temperature. The reaction mixture was refluxed for 30 minutes and poured into water and the organic layer separated, washed and dried. Crude material (6.8 g., 75% yield) was obtained. Gas chromatography showed the presence of one main product in this crude material. It was separated by preparative v.p.c. and identified as $CFClBrCFClCH=CH_2$, b.p. 144° (micro), n_D^{21} 1.4571, d_4^{21} 1.7209 (I.R. C=C 6.1μ) (Anal. Calcd. for $C_4BrCl_2F_2H_3$: Br, 33.30. Found: Br, 33.29%). The H^1 and F^{19} n.m.r. spectra were consistent with the above structure.

4. Dehalogenation of $CFClBrCFClCH_2CH_2Br$ with zinc

$CFClBrCFClCH_2CH_2Br$ (16.1 g., 0.05 mole) was dropped slowly into a mixture of zinc (6.5 g., 0.1 g. atom), ethanol (4.6 g., 0.1 mole) and zinc chloride (0.1 g., 0.001 mole) at reflux temperature. The reaction mixture was refluxed for 30 minutes and the low boiling material (12.9 g.) was distilled directly from the reaction mixture. Gas chromatography showed the presence of one new main product in this material. This was separated by preparative v.p.c. and identified as an isomeric mixture of cis (44%) and trans (56%), $CFCl=CF-CH_2CH_2Br$, b.p. 138° (micro),

n_D^{21} 1.4514, d_4^{21} 1.6808 (I.R. C=C 5.76μ) (Anal. Calcd. for $C_4BrClF_2H_4$: Br, 38.94; Cl, 17.27. Found: Br, 38.82; Cl, 17.40%). The H^1 and F^{19} n.m.r. spectra were consistent with the above structure.

5. Dehydrohalogenation of $CFCl=CFCH_2CH_2Br$ with potassium hydroxide

$CFCl=CFCH_2CH_2Br$ (5 g., 0.025 mole) was dropped slowly into a mixture of potassium hydroxide (5.6 g., 0.1 mole) and ethanol (4.6 g., 0.1 mole).

The low boiling material (2.4 g., 80% yield) distilled directly from the reaction mixture as it was formed. Gas chromatography showed the presence of one new main product in this material. This was separated by prep. v.p.c. and identified as an isomeric mixture of cis (44%) and trans (56%) $CFCl=CF-CH=CH_2$, which polymerizes on standing at room temperature (Anal. Calcd. for $\left[C_4ClF_2H_3\right]_n$: Cl, 27.68. Found: Cl, 28.29%). The H^1 and F^{19} n.m.r. spectra were consistent with the above structure.

Addition of CF_2BrCF_2Br to Olefins and Dehydrohalogenation of the Addition Products

1. Addition to ethylene

CF_2BrCF_2Br (401 g., 1.54 mole), ethylene (17.5 g., 0.63 mole) and benzoyl peroxide (2.5 g., 0.01 mole) were heated in an autoclave at 100° for 12 hours with constant rocking. On venting the autoclave 0.5 g. low boiling material (mostly ethylene) was condensed. Gas

chromatography showed the presence of two new main products in the residual liquid. Distillation yielded 57 g. (32% yield) of 1:1 adduct, $CF_2BrCF_2CH_2CH_2Br$, b.p. 72°/80 mm., n_D^{21} 1.4167, d_4^{21} 1.9702 (Anal. Calcd. for $C_4Br_2F_4H_4$: Br, 55.56. Found: Br, 55.81%) and 38.5 g. (20% yield) of 2:1 adduct, $CF_2BrCF_2(CH_2)_3CH_2Br$, b.p. 76°/10 mm., n_D^{21} 1.4337, d_4^{21} 1.7902 (Anal. Calcd. for $C_6Br_2F_4H_8$: Br, 50.63. Found: Br, 50.41%). The H^1 and F^{19} n.m.r. spectra were consistent with the above structures.

2. Dehydrohalogenation of $CF_2BrCF_2CH_2CH_2Br$ with potassium hydroxide

$CF_2BrCF_2CH_2CH_2Br$ (21.7 g., 0.075 mole) was dropped slowly into a mixture of KOH (8 g., 0.14 mole) and ethanol (23 g., 0.5 mole) at reflux temperature. The olefin (15.2 g., 96% yield) was distilled directly from the reaction mixture as it was formed. This was purified by preparative v.p.c. and identified as $CF_2BrCF_2CH=CH_2$, b.p. 54.5°, n_D^{21} 1.3556, d_4^{21} 1.6042 (I.R. C=C 6.06μ) (Anal. Calcd. for $C_4BrF_4H_3$: Br, 38.65. Found: Br, 38.44%). The H^1 and F^{19} n.m.r. spectra were consistent with the above structure.

3. Dehydrohalogenation of $CF_2BrCF_2(CH_2)_3CH_2Br$ with potassium hydroxide

$CF_2BrCF_2(CH_2)_3CH_2Br$ (9.6 g., 0.03 mole) was dropped slowly into a mixture of KOH (5.6 g., 0.1 mole), ethanol (9.2 g., 0.2 mole) and water (9 g., 0.5 mole) at reflux

temperature. The reaction mixture was kept at reflux temperature for another 30 minutes and it was poured into water. The organic layer was separated, washed and dried. Gas chromatography showed the presence of two new main products in this material. Their amounts were estimated by v.p.c. analysis. They were separated by preparative v.p.c. and identified as $CF_2BrCF_2(CH_2)_2CH=CH_2$ (1.0 g., 14% yield), b.p. 119.5° (micro), n_D^{21} 1.3851 (I.R. C=C 6.07μ) (Anal. Calcd. for $C_6BrF_4H_7$: Br, 34.02. Found: Br, 33.22%) and $CF_2BrCF_2(CH_2)_3CH_2OCH_2CH_3$ (5.7 g., 67% yield), b.p. 185.7° (micro), n_D^{21} 1.3964, d_4^{21} 1.3670 (Anal. Calcd. for $C_8BrF_4H_{13}O$: Br, 28.48. Found: Br, 28.34%). The H^1 and F^{19} n.m.r. spectra were consistent with the above structures.

4. Addition to chlorotrifluoroethylene

CF_2BrCF_2Br (176 g., 0.68 mole), $CF_2=CFCl$ (21 g., 0.02 mole) and benzoyl peroxide (1 g., 0.004 mole) were heated in an autoclave at 100° for 12 hours with constant rocking. On venting the autoclave no low boiling material was obtained. Gas chromatography showed the absence of any new high boiling material in the reaction mixture.

5. Addition to allyl ethyl ether

CF_2BrCF_2Br (55 g., 0.2 mole), allyl ethyl ether (8 g., 0.1 mole) and benzoyl peroxide were heated in a sealed tube at 100° for 16 hours. Gas chromatography showed the

absence of any new high boiling material in the reaction mixture.

Addition of $CF_2BrCFBrCF_3$ to Olefins and Dehydrohalogenation of the Addition Product

1. Addition to ethylene

$CF_2BrCFBrCF_3$ (236 g., 0.76 mole), ethylene (7 g., 0.25 mole) and benzoyl peroxide (1 g., 0.004 mole) were heated in an autoclave at 100° for 16 hours with constant rocking. On venting the autoclave no low boiling material was obtained. Gas chromatography showed the presence of one new main product in the reaction mixture. Distillation yielded 43 g. (51% yield) of 1:1 addition product, $CF_2BrCF(CF_3)CH_2CH_2Br$, b.p. 145° (micro), n_D^{21} 1.4017, d_4^{21} 1.992 (Anal. Calcd. for $C_5Br_2F_6H_4$: Br, 47.34. Found: Br, 47.34%). The H^1 and F^{19} n.m.r. spectra were consistent with the above structure.

2. Dehydrohalogenation of $CF_2BrCF(CF_3)CH_2CH_2Br$ with potassium hydroxide

$CF_2BrCF(CF_3)CH_2CH_2Br$ (20.2 g., 0.065 mole) was dropped slowly into a mixture of KOH (7 g., 0.13 mole) and ethanol (4.6 g., 0.1 mole) at room temperature. The reaction mixture was refluxed for 1 hour and poured into water. The organic layer was separated, washed and dried. Crude material (8 g., 54% yield) was obtained. Gas chromatography showed the presence of one new main product in

this material. This was separated by preparative v.p.c. and identified as $CF_2BrCF(CF_3)CH=CH_2$, b.p. 79° (micro), n_D^{21} 1.3469, d_4^{21} 1.663 (I.R. C=C 6.08μ) (Anal. Calcd. for $C_5BrF_6H_3$: Br, 31.17. Found: Br, 31.58%). The H^1 and F^{19} n.m.r. spectra were consistent with the above structure.

3. Addition to allyl chloride

$CF_2BrCFBrCF_3$ (254 g., 0.82 mole), allyl chloride (38.5 g., 0.50 mole) and benzoyl peroxide (1 g., 0.004 mole) were heated in an autoclave at 100° for 12 hours with constant rocking. On venting the autoclave no low boiling material was obtained. Gas chromatography showed the absence of any new higher boiling material in the reaction mixture.

4. Addition to allyl ethyl ether

$CF_2BrCFBrCF_3$ (61.5 g., 0.2 mole), allyl ethyl ether (10 g., 0.12 mole) and benzoyl peroxide (0.5 g., 0.002 mole) were heated in a sealed tube at 100° for 16 hours. Gas chromatography showed the absence of any new higher boiling material in the reaction mixture.

Preparation and Addition of $CF_3CFBrCFBrCF_3$ to Ethylene

1. Preparation of $CF_3CFBrCFBrCF_3$

$CF_3CFBrCFBrCF_3$ was made by bromination of $CF_3CF=CFCF_3$.

2. Addition to ethylene

$CF_3CFBrCFBrCF_3$ (346 g., 0.96 mole), ethylene (14.5 g., 0.52 mole) and benzoyl peroxide (5 g., 0.02 mole) were heated at 100° for 8 hours with constant rocking. On venting the autoclave 30 g. low boiling material was obtained. This consisted of ethylene and perfluorobutene-2. Gas chromatography showed the presence of two new materials in the reaction mixture. Their yields were estimated by distillation and v.p.c. analysis. They were identified as $CF_3CF=CFCF_3$ (40 g., 20% yield), b.p. 2° (Lit.[22] b.p. 0°/740 mm.) and CH_2BrCH_2Br (37 g., 20% yield), b.p. 131° (micro), n_D^{21} 1.5375, d_4^{21} 2.1685 (Lit.[23] b.p. 131.6°, n_D^{25} 1.5379, d_4^{25} 2.1701).

Preparation and Addition of $CF_3CFBrCClBrCF_3$ to Ethylene

1. Preparation of $CF_3CFBrCClBrCF_3$

$CF_3CFBrCClBrCF_3$ was prepared from $CF_3CFClCCl_2CF_3$ by dechlorination followed by bromination of the product.[24]

2. Addition to ethylene

$CF_3CFBrCClBrCF_3$ (242 g., 0.64 mole), ethylene (7 g., 0.25 mole) and benzoyl peroxide (3 g., 0.012 mole) were heated in an autoclave at 100° for 4 hours with constant rocking. On venting the autoclave 50 g. low boiling material was condensed. This consisted of $CF_3CF=CClCF_3$ with small amount of ethylene. Gas chromatography showed

the presence of only one new main product in the residual mixture. This was identified as CH_2BrCH_2Br as described in the previous experiment. Distillation and v.p.c. analsis showed a quantitative yield of $CF_3CF=CClCF_3$ and CH_2BrCH_2Br.

Preparation and Addition of 1,2-Dibromoperfluorocyclobutane to Olefins

1. Preparation of 1,2-dibromoperfluorocyclobutane

1,2-Dibromoperfluorocyclobutane was prepared by the cyclic dimerization of bromotrifluoroethylene by the method used for the similar dimerization of chlorotrifluoroethylene.[25]

2. Addition to ethylene

1,2-Dibromoperfluorocyclobutane (83 g., 0.26 mole), ethylene (5 g., 0.2 mole) and benzoyl peroxide (1 g., 0.004 mole) were heated in an autoclave at 100° for 12 hours with constant rocking. On venting the autoclave an almost quantitative amount of ethylene was condensed. Gas chromatography showed the absence of any new product in the residual reaction mixture.

3. Addition to 1,3-butadiene

1,2-Dibromoperfluorocyclobutane (68 g., 0.21 mole), 1,3-butadiene (9 g., 0.16 mole) and benzoyl peroxide (1 g., 0.004 mole) were heated in an autoclave at 100° for 12 hours with constant rocking. On venting the autoclave

an almost quantitative amount of 1,3-butadiene was condensed. Gas chromatography showed the absence of any new product in the residual reaction mixture.

Addition of $CF_2BrCHFBr$ to Ethylene

$CF_2BrCHFBr$ (297 g., 1.13 mole), ethylene (9 g., 0.32 mole) and benzoyl peroxide (1.5 g., 0.006 mole) were heated in an autoclave at 100° for 12 hours with constant rocking. On venting the autoclave an almost quantitative amount of ethylene was condensed. Gas chromatography showed the absence of any higher boiling material in the residual reaction mixture.

Preparation and Addition of $CH_2=CHI$ to Tetrafluoroethylene

1. Preparation of vinyl iodide

$CH_2=CH_2$ (28 g., 1 mole), iodine (298 g., 1.17 mole) and $CHCl_3$ (90 g., 0.75 mole) were heated in an autoclave at 150° for 8 hours with constant rocking. On venting the autoclave no gaseous material was obtained. The dark colored residual liquid was washed with a saturated solution of sodium thiosulfate, dried and evaporated to dryness to give a slightly colored solid (200 g.). This was heated with KOH (100 g., 1.79 mole) in mineral oil and the volatile material was distilled, under reduced pressure, out of the reaction flask as it was formed. Redistillation

yielded 50 g. (33% yield) of vinyl iodide, b.p. 56° (Lit.[23] b.p. 56°). The H^1 n.m.r. spectra was consistent with the above structure.

2. Addition to tetrafluoroethylene

CH_2=CHI (24 g., 0.16 mole), tetrafluoroethylene (13 g., 0.13 mole) and benzoyl peroxide (0.5 g., 0.002 mole) were heated in an autoclave at 100° for 4 hours. On venting the autoclave 12.5 g. low boiling material (mostly tetrafluoroethylene) was condensed. Gas chromatography showed the absence of any new high boiling material in the residual mixture.

Preparation and Addition of CF_2ICF_2I to Olefins

1. Preparation of CF_2ICF_2I

CF_2ICF_2I was prepared by the addition of iodine to tetrafluoroethylene, as reported in the literature.[20]

2. Addition to ethylene

CF_2ICF_2I (352 g., 1 mole), ethylene (16.2 g., 0.58 mole) and benzoyl peroxide (1.5 g., 0.006 mole) were heated in an autoclave at 100° for 12 hours with constant rocking. On venting the autoclave 20 g. low boiling material (mostly ethylene) was condensed. Gas chromatography showed the presence of one new product ($<2\%$ yield) in the residual mixture. This could not be isolated by distillation. The residue left, after most of the CF_2ICF_2I was

distilled off, was treated with alcoholic KOH. Gas chromatography showed the presence of dehydrohalogenation product, but this was in insufficient quantity to be isolated.

3. Addition to ethylene

CF_2ICF_2I (142 g., 0.40 mole) and ethylene (16 g., 0.57 mole) were heated in an autoclave at 220° for 7 hours with constant rocking. On venting the autoclave no low boiling or liquid product was obtained. Only dark colored solid material was obtained. This was insoluble in acetone and alcohol. No liquid product was obtained when this solid material was heated with alcoholic potassium hydroxide.

4. Addition to allyl chloride

CF_2ICF_2I (70.6 g., 0.2 mole), allyl chloride (7.6 g., 0.1 mole) and benzoyl peroxide (0.5 g., 0.001 mole) were heated in a Fischer-Porter tube at 100° for 8 hours. Gas chromatography showed the absence of any new product in the reaction mixture.

Addition of $CH_2=CHCH_2I$ to Tetrafluoroethylene

$CH_2=CHCH_2I$ (108 g., 0.6 mole), tetrafluoroethylene (38 g., 0.38 mole) and benzoyl peroxide (1 g., 0.004 mole) were heated in an autoclave at 100° for 8 hours with constant rocking. On venting the autoclave 17 g. low boiling

material (mostly tetrafluoroethylene) was condensed. Gas chromatography showed the presence of four new products in the residual mixture. Their proportions were estimated by v.p.c., separated by preparative scale v.p.c., and were identified as follows:

I. CH_3CHICH_3 (10.5 g., 28% yield), b.p. 89° (micro), n_D^{21} 1.4996, d_4^{21} 1.667 (Lit.[23] b.p. 89.5°, n_D^{20} 1.4996, d_4^{20} 1.703) (Anal. Calcd. for C_3H_7I: C, 21.09; H, 4.12; I, 74.8. Found: C, 21.43; H, 4.29; I, 73.11%).

II. $CH_2=CHCH_2CF_2CF_2CH_2CH=CH_2$ (2.6 g., 6% yield), b.p. 118° (micro), n_D^{21} 1.3721 (I.R. C=C 6.08μ) (Anal. Calcd. for $C_8F_4H_{10}$: C, 52.75; H, 5.49; F, 41.76. Found: C, 52.33; H, 5.31; F (by difference), 42.36%).

III. $CH_2=CHCH_2CF_2CF_2I$ (19.5 g., 34% yield), b.p. 114° (micro), n_D^{21} 1.4188 (I.R. C=C 6.09μ) (Anal. Calcd. for $C_5F_4H_5I$: C, 22.39; H, 1.87; I, 47.78. Found: C, 22.93; H, 1.99; I, 47.65%).

IV. CF_2ICF_2I (13.7 g., 17.5% yield), b.p. 108.5°, n_D^{21} 1.4892, d_4^{21} 2.581 (Lit.[22] b.p. 112-3°; n_D^{25} 1.4895; d_4^{25} 2.6293) (Anal. Calcd. for $C_2F_4I_2$: C, 6.91; H, 0.0; I, 71.80. Found: C, 7.81; H, 0.22; I, 70.24%). The H^1 and F^{19} n.m.r. spectra were consistent with the above structures.

SUMMARY

A detailed study was made on the free radical addition of perhaloalkanes to olefins in the presence of benzoyl peroxide. Dehydrohalogenation and dehalogenation of the various adducts gave several new unsaturated compounds.

It was found that the perhaloalkanes, $CF_3CF_2CCl_3$, $CF_2ClCF_2CCl_3$, $CFClBrCFClBr$, CF_2BrCF_2Br, $CF_2BrCFBrCF_3$, $CCl_3CF_2CFClBr$ and $CCl_3CF_2CF_2Br$ add to certain olefins while $C_6H_5CCl_3$, $CFCl_2CFCl_2$, $CF_3CFBrCFBrCF_3$, $CF_3CFBrCClBrCF_3$, 1,2-dibromoperfluorocyclobutane, $CF_2BrCFHBr$ and CF_2ICF_2I do not add under similar conditions. Generally, these perhaloalkanes do not add to allyl chloride, chlorotrifluoroethylene and allyl ethyl ether. It was also found that vinyl iodide does not add to tetrafluoroethylene while the addition of allyl iodide to tetrafluoroethylene gave a good yield of CH_3CHICH_3, $(CH_2=CHCH_2CF_2)_2$ and $CH_2=CHCH_2CF_2CF_2I$ under similar conditions.

A study on the addition of CCl_3Br to tetrafluoroethylene and perfluorocyclobutene showed that it adds only to tetrafluoroethylene. No 1:1 adduct was formed in the addition of $CF_2BrCFClBr$ to acrylonitrile.

On dehydrohalogenation the addition products of $CCl_3CF_2CF_3$ and $CCl_3CF_2CF_2Cl$ to olefins gave several new unsaturated compounds, while the addition products from other perhaloalkanes gave the expected olefins. For example, the addition product, $CF_2ClCF_2CCl_2CH_2CCl(CH_3)_2$, on dehydrohalogenation gave seven products. The first three could not be isolated and v.p.c. analysis indicated them to be the isomeric olefins, $CF_2ClCF_2CCl_2CH_2C(CH_3)=CH_2$, $CF_2ClCF_2CCl_2CH=C(CH_3)_2$, and $CF_2ClCF_2CCl=CHCCl(CH_3)_2$ while the other four were identified as $CF_2ClCF_2CCl=CHC(CH_3)=CH_2$, $CF_2ClCF_2CCl=C=C(CH_3)_2$, $CF_2ClCF_2C\equiv CCCl(CH_3)_2$, and $CF_2ClCF_2C\equiv CC(CH_3)=CH_2$.

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BIOGRAPHICAL SKETCH

Jai Prakash Tandon was born July 15, 1937, in Sambhal, U. P., India. He attended public school in Sambhal, U. P., India, and was graduated from Hind Inter College, Sambhal, in June, 1953.

In July, 1953, he entered S. M. College, Chandausi, U. P., India,and was graduated from there in June, 1956, with an Intermediate in Science diploma of U. P. Board, India. The same year, in July, he entered the Agra University, U. P., India. The author was graduated in the first division with a Bachelor of Science degree with major in Chemistry, Physics and Mathematics in June, 1958.

The following July he enrolled in the Graduate School of the Banaras Hindu University, Banaras, U. P., India. The author was graduated in the first division with a Master of Science degree with major in Physical Chemistry in June, 1960. He continued his studies there toward the degree of Doctor of Philosophy until December, 1960; then he joined the staff of Banaras Hindu University as a lecturer and taught freshman Chemistry until December, 1961. In January, 1962, he was awarded a predoctoral fellowship by C. S. I. R., New Delhi, India, and he again

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The following September he came to the U. S. A. and enrolled in the Graduate School of the University of Florida as a graduate teaching assistant. In September, 1964, he received a predoctoral fellowship supported by the U. S. Army Natick Laboratories, Natick, Massachusetts. He has held this position continuously until the present time.

The author is married to the former Nirmal Mehrotra of Nawabganj, U. P., India, and has one son.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August 13, 1966

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